

Characterization of Adhesion Promoter Films Using PEEM and SPEM

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INTRODUCTION

Adhesion promoters (APs) are used in various applications including a) compatibilizing glass fibers with polymer matrices to increase the strength of composite materials, b) adhering rearview mirrors to automotive windshields, c) enhancing the adhesion of polymers to metal surfaces, d) modifying the wettability of various surfaces and e) controlling the biocompatibility of surfaces. Although these materials have been known at least since the 1940s [1], and have been extensively studied by advanced surface science techniques [2-5], there are still many remaining questions about the microscopic structure and mode of action both in service and in failure. Our particular interest here is in the use of adhesion promoters to enhance the adhesion of low dielectric, thin polymer films for electronic applications such as interlayer dielectrics, multichip modules, and packaging [5]. The x-ray photoemission electron microscope (XPEEM or PEEM) on beamline BL7.3.1.1 and the scanning photoelectron microscope (SPEM) on BL 7.0.1 are new tools, which we are finding to be particularly useful in understanding the surface chemistry of these very versatile materials.

Adhesion promoters often have the generalized chemical formula: $G-Si(OR)_3$, where the R groups can be methyl, ethyl, acetate or other. The R group is hydrolyzed (usually in solution prior to application) and the resulting siloxyl group is understood to react with free hydroxyl groups on the surface of interest. The G group consists of a moiety with favorable interaction with the polymer or organic phase. The adhesion promoters can be applied by spin casting, dipping or vapor dosing. We have begun using XPEEM and SPEM in combination with atomic force microscopy (AFM) to determine the degree of coverage of spin coated adhesion promoter films on various substrate surfaces. In the example discussed below, the AP used was Dow's AP 3000 which is used with the Photo-BCB based thin film dielectric polymers for electronic packaging and contains as the active ingredient, vinyltriacetoxysiloxane. It was prehydrolyzed before adding it to a solvent; the prehydrolysis also results in a condensation polymerization of the AP producing moderate increase in molecular weight of the AP. The AP solution was then spin-coated onto the Si substrates and heated to 100 or 180° C [5].

SPEM, PEEM and AFM images are compared in Figure 1. Three SPEM images of the as-spun, not heated, surface are shown. These were acquired using the electron analyzer to accept C(1s) or Si(2p) electrons or by measuring the total electron yield (absorbed sample current). The PEEM and AFM images presented compare images for the three different heating schedules.

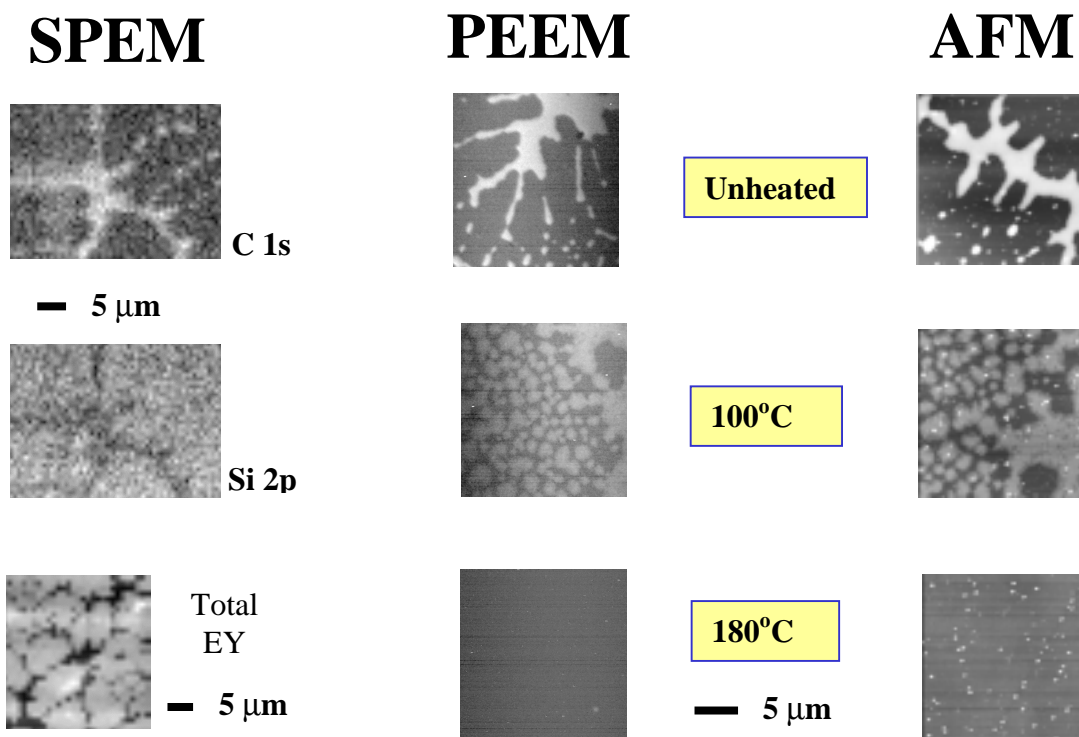


Figure 1. Comparison of images of the adhesion promoter covered Si (111) surfaces from SPEM, PEEM and AFM microscopies. The SPEM images were of the as-spun, not heated, sample only and acquired using C(1s), Si(2p) and total electron yield electrons. The small white spots on the AFM image of the 180° sample are thought to be due to contamination during the imaging and not representative of the clean surface.

The most obvious observation one makes is that all three techniques show similar structure on the surface of the sample prior to the heat treatment. This structure consists of ridges of material with occasional disconnected mounds of varying lateral size. AFM indicates the height of the ridges on the as-spun sample average about 11 nm and about 3 nm on the surface heated to 100° C. The surface heated to 180° C was very smooth lacking any obvious structure greater than 0.1 nm. The C(1s) and Si(2p) SPEM images, which show the mounds as white and dark respectively, indicate that the mounds are high in C and low in Si. The high resolution Si(2p) x-ray photoelectron spectra (not shown) have two peaks which can be assigned to elemental Si which is more intense between the mounds and oxidized Si (either SiO_x on the substrate surface or the Si in the adhesion promoter which is bonded to three O atoms).

Despite the dramatic structure of the adhesion promoter films, this adhesion promoter system provides very good adhesion of polymer to the substrate compared to films made without promoter [5]. This latter result seemed at odds with the observed heterogeneity of the AP films, so we used PEEM to try to understand this issue. By measuring many images at different energies, one can determine the surface NEXAFS spectrum at every pixel of the images (called stack images) [6]. We used the stack images to determine the spectrum on and off the ridges of material for this sample series (Figure 2). In Figure 2, the spectra are offset vertically for ease of comparison, but are not normalized in intensity. These spectra indicate several important points: 1. The as-made film consists of a continuous film of AP with ridges of thicker AP. 2. The vinyl group (indicated by the

$\pi^*(C=C)$ peak) does not appear to be affected by the heat treatment. 3. The thickness of AP on the surface decreases with increasing heating temperature. 4. A thin layer of AP appears to remain on the surface even after the 180° C treatment.

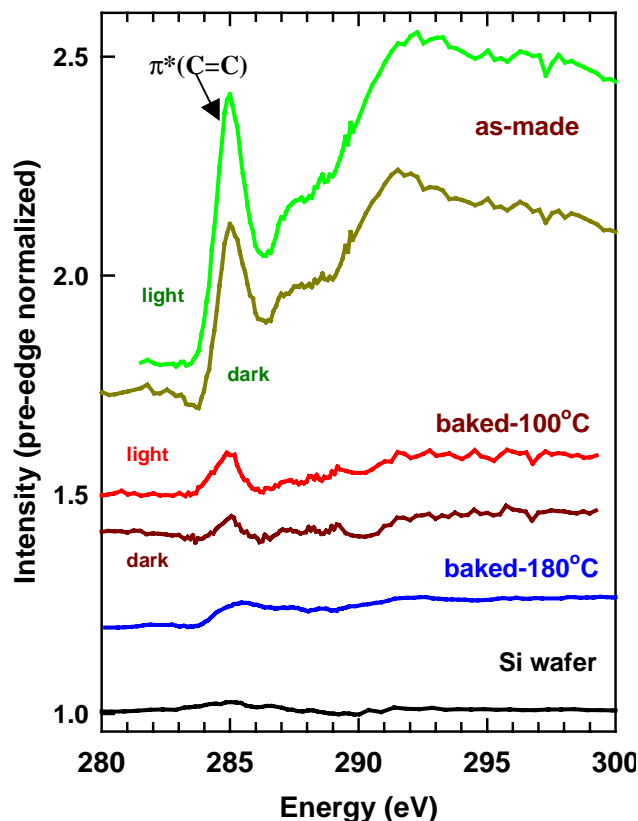


Figure 2. NEXAFS spectra of the adhesion promoter films acquired using the PEEM in image stack mode.

These results then appear to explain why this particular AP formulation works so well, despite the apparent heterogeneity of the AP films. Because there is AP everywhere on the surface, molecular bonding can occur between the surface and the overlaying polymer film uniformly across the surface. Despite the loss of some AP during baking to 180° C, a thin layer of adhesion promoter is still present to again provide adequate bonding. We are continuing to use PEEM to understand the different AP formulation parameters, which influence the structure of the AP films and to understand the effects of heating, oxidation, solvent rinsing and other process parameters.

The high surface sensitivity, good chemical specificity and superb lateral spatial resolution of PEEM and SPEM make these techniques uniquely suited to determining the lateral homogeneity of adhesion promoter films down to the limit of resolution (~50 nm for PEEM and currently ~150 nm for SPEM).

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